

Ab initio modeling of ligand adsorption on colloidal CuInS₂ quantum dots

Colloidal quantum dots (QDs) have gained widespread interest in recent years for their tunable optoelectronic properties. Applications range from usage as biomedical markers to the creation of tunable LEDs and improving solar cell efficiency. During synthesis these QDs are surrounded by a capping of organic ligands. Since these ligands influence the QD growth, morphology and functionality, understanding and quantifying the nanocrystal/ligand interaction is critical for QD research. Here, we present a theoretical study on the ligand-QD interaction of CuInS₂ (CIS) QDs. CIS is less toxic than currently used Cd- and Pb-based QDs, making it viable for mass usage, while providing similar physical properties. We calculate the ligand adsorption energy using ab initio simulations based on periodic Density Functional Theory. For sufficiently large QDs the surface consists of facets matching the bulk crystal planes. Since ligands can have different affinities for different facets, each facet is modeled as a separate slab on which ligand models representative of amines, carboxylic acids and thiols are then adsorbed. Comparing the adsorption energies thus obtained shows the influence of surface morphology and allows for a comparison between the three species. For example simulations on a reconstructed (001) surface reproduce the experimental trend in adsorption to the QD surface with amines adsorbing strongest (around 30 kJ/mol) while carboxylic acids and thiols adsorb much weaker.